

Coherent storage of photoexcited triplet states using ^{29}Si nuclear spins in silicon

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Pulsed electron paramagnetic resonance spectroscopy of the photoexcited, metastable triplet state of the oxygen-vacancy center in silicon reveals that the lifetime of the $m_s = \pm 1$ sub-levels differ significantly from that of the $m_s = 0$ state. We exploit this significant difference in decay rates to the ground singlet state to achieve nearly $\sim 100\%$ electron spin polarization within the triplet. We further demonstrate the transfer of a coherent state of the triplet electron spin to, and from, a hyperfine-coupled, nearest-neighbor ^{29}Si nuclear spin. We measure the coherence time of the ^{29}Si nuclear spin employed in this operation and find it to be unaffected by the presence of the triplet electron spin and equal to the bulk value measured by nuclear magnetic resonance.

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Nuclear spins in solids are promising candidates for quantum bits (qubits) as their weak coupling to the environment often leads to very long spin coherence times [1–4]. However, performing fast manipulation and controlling interaction between nuclear spin qubits is often more challenging than in other, more engineered, quantum systems [5–7]. The use of an optically driven mediator spin has been suggested as a way to control coupling between donor electron spins in silicon: the donor spins exhibit weak direct coupling, but mutually couple through the optically excited state of the mediator [8]. Such ideas could similarly be applied to couple nuclear spins, and, if the mediator spin is a photo-excited triplet with a spin-zero single ground state, it would have the added advantage that it avoids long-term impact on the nuclear spin coherence [9–11].

Photoexcited triplets are optically-generated electron spins ($S = 1$) which often exhibit large (positive or negative) spin polarization, thanks to preferential population of each of the triplet sub-levels following intersystem crossing and/or the differing decay rates of these sub-levels to the ground singlet state [12, 13]. Nuclear spins, in contrast, have weak thermal spin polarization at experimentally accessible conditions, due to its small magnetic moment. Highly polarized electron spin triplets can be used to polarize surrounding nuclear spins, through continuous wave microwave illumination (under processes termed dynamic nuclear polarization) [14, 15], or using microwave pulses [16]. Triplet states can also be used to mediate entanglement between mutually-coupled nuclear spins [9], on timescales much faster than their intrinsic dipolar coupling [17].

Oxygen-vacancy (O-V) complexes can be formed in silicon by electron beam or γ -ray irradiation of oxygen-rich silicon crystals [18, 19], and can be excited to the triplet

state (termed an SL1 center,) using illumination of above band gap light [20]. Magnetic resonance studies including electron paramagnetic resonance (EPR), electrically or optically detected magnetic resonance, spin dependent recombination and electrically-detected cross relaxation [20–25] have revealed that the SL1 has orthorhombic symmetry with non-equilibrium triplet electron spin polarization and strong hyperfine coupling with the nearest neighbor ^{29}Si nuclear spins. The triplet spin polarization of SL1 centers can be incoherently transferred to bulk ^{29}Si nuclear spins in the lattice by all-optical methods [26] or dynamic nuclear polarization [27, 28]. Previous electron spin echo studies on SL1 performed at zero magnetic field have revealed that the populating rates of the triplet sub-levels are equal, and the spin polarization arises instead from a difference in the decay rates to the singlet ground state [29]. In this Letter we use the high spin polarization of the triplet system and its strong coupling with the nearest neighbor ^{29}Si nuclear spins to demonstrate coherent state transfer between the electron and nuclear spin degrees of freedom, and examine the nuclear spin coherence in the presence of the triplet.

Cz-grown, single-crystal natural silicon (4.7% ^{29}Si , $I = 1/2$) was exposed to 1 MeV e-beam irradiation (dose $\approx 10^{18} \text{ cm}^{-2}$) at room-temperature to form O-V complexes (an interstitial oxygen already present in the silicon traps a mono-vacancy generated due to the e-beam irradiation). Pulsed EPR measurements were carried out at X-band (9.72 GHz) on a Bruker Elexsys580 spectrometer equipped with a helium-flow cryostat. Photoexcitation of the SL1 was achieved using a 1064 nm pulsed Nd:YAG laser (pulse width $\sim 7 \text{ ns}$, 1 mJ/pulse) with a 10 Hz repetition rate.

Figure 1a illustrates the SL1 center in silicon under two representative orientations of the static magnetic field

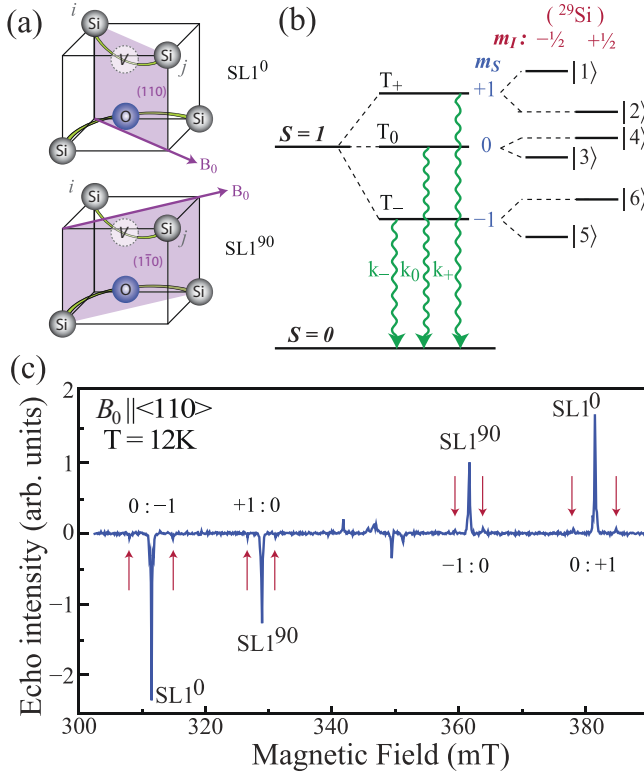


FIG. 1: (color online). (a) Structures of the oxygen-vacancy centre in silicon, illustrating the SL1⁰ and SL1⁹⁰ orientations with respect to the externally applied magnetic field B_0 . (b) The SL1 triplet ($S = 1$) state is Zeeman split by B_0 into levels T_+ , T_0 , and T_- . These states decay with different rates (k_+ , k_0 , and k_- , respectively) to the ground singlet ($S = 0$) state. The hyperfine coupling to the ^{29}Si ($I = 1/2$) nuclear spin at lattice site i or j further splits the triplet states. (c) Electron spin echo-detected EPR spectrum of the SL1 center at 12 K with $B_0 \parallel \langle 110 \rangle$. The satellite peaks (red arrows) arise from hyperfine coupling to ^{29}Si .

B_0 . Under one orientation, termed SL1⁰, the magnetic field lies in the plane, marked (110), comprising the oxygen atom and two vacancy-trapping silicon atoms (i and j lattice sites). An alternative orientation (SL1⁹⁰) has the magnetic field in an orthogonal plane (1 $\bar{1}$ 0) with respect to the same center. Both planes are equivalent by symmetry for the crystal as a whole, so both orientations are visible in the EPR spectrum.

Figure 1b shows the triplet energy sub-levels in the presence of a static magnetic field (T_+ , T_0 , and T_-), each of which decays with a characteristic rate to the ground singlet state [24, 30]. The hyperfine coupling with one of the two nearest-neighbor ^{29}Si nuclear spins (occupying i or j lattice site) further splits the $T_{\pm 1}$ sub-levels, while the T_0 state ($m_s = 0$) has no first-order hyperfine interaction, thus the nuclear spin splitting in this sub-level is close to the Zeeman energy of ^{29}Si . The EPR spectrum obtained by monitoring the electron spin echo intensity

as a function of magnetic field at 12 K with $B_0 \parallel \langle 110 \rangle$ is shown in Fig. 1c, labeled with electronic transitions identified by previous cw-EPR studies [20]. The satellite peaks accompanying each main peak are due to the hyperfine interaction with the ^{29}Si nuclear spins situated at i or j lattice sites. The phase difference of the spin echo (i.e. dips or peaks) is indicative of the non-equilibrium polarization within the electron spin triplet.

To investigate the origin of this non-equilibrium polarization, we studied the decay kinetics of the triplet by measuring the electron spin echo at a variable time T after the optical excitation ($h\nu$ - T - $\pi/2$ - π - τ - π - τ -echo), as shown in Fig. 2a. The zero echo intensity at $T = 0$ indicates equal initial filling of the three triplet sub-levels upon creation of the triplet. The echo intensity proceeds to grow as T is increased. This can be attributed to a difference in the decay rates of the triplet sub-levels to the ground state, creating a build-up in spin polarisation (positive or negative) across the EPR transition being measured.

Based on the simple decay model shown in Fig. 1b, the population difference between a given pair of sub-levels follows a biexponential behavior where the two time constants represent the lifetimes of the two sub-levels involved in the EPR transition. The time constants obtained from biexponential fitting to the FD curves are given in Table I — the assignment of rates to particular energy levels is enabled by electron nuclear double resonance experiments described further below. As the transition from the triplet to the ground singlet is determined by the amount of singlet admixture to the triplet via spin-orbit coupling, the lifetimes are expected to depend on the defect orientation with respect to the magnetic field. The composition of triplet levels $T_{+,0,-}$ can be expressed in terms of the zero-field eigenstates ($T_{x,y,z}$), and similarly the observed decay rates from these levels can be traced back to a corresponding mixture of zero-field decay rates ($k_{x,y,z}$), as shown in Table 1. These values are in good agreement with times measured using zero-field EPR [29].

Our model assumes that there is negligible spin-lattice relaxation within the triplet sub-levels, and this is consistent with lack of temperature dependence we observe in the relaxation dynamics below 20 K. Nevertheless, in order to probe the dynamics in more detail, we can introduce an additional inversion π pulse to the sequence: ($h\nu$ - T_X - π - T_Y - $\pi/2$ - π - τ - π - τ -echo). Figure 2c shows the 2D plot of the echo intensity for this sequence, as both T_X (the delay after the laser pulse) and T_Y (the delay after the inversion pulse) are varied. The simulation of this experiment, based on the model described above, is in good agreement with the observed behavior, supporting our assumption that spin-lattice relaxation can be neglected.

Based on the observed decay rates, we can extract both the polarization buildup (Fig. 2d) and the triplet

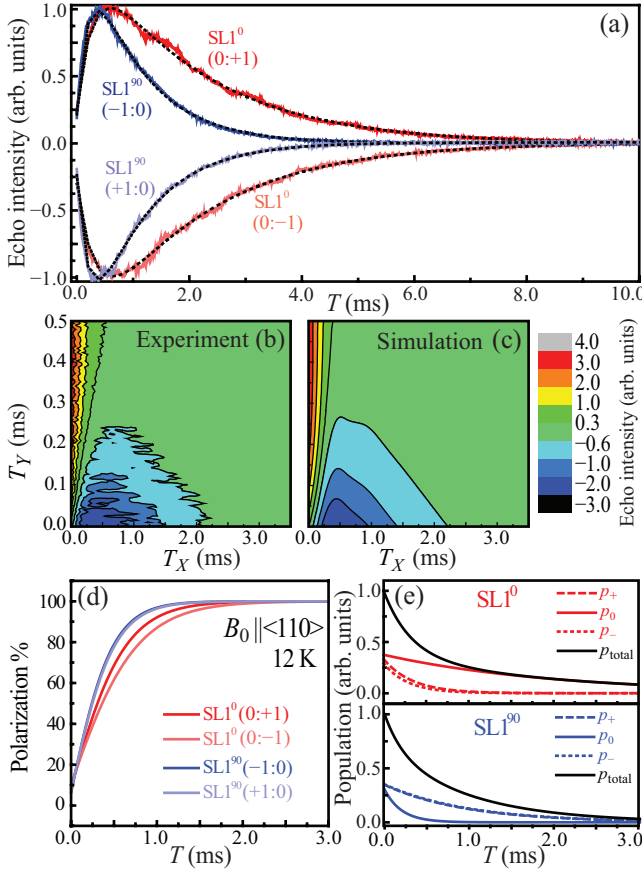


FIG. 2: (color online). (a) Decay traces obtained by the flash delay ($h\nu-T-\pi/2-\tau-\pi-\tau-echo$) pulse sequence, used to extract the triplet decay rates shown in Table I. (b) Experimental and (c) simulated 2D plots of the decay characteristics observed with the pulse sequence $h\nu-T_X-\pi-T_Y-\pi/2-\tau-\pi-\tau-echo$. (d) The polarization build-up and (e) triplet population as a function of waiting time T after the laser pulse.

population (Fig. 2e) for the two $SL1$ orientations ($SL1^0$ and $SL1^{90}$) as a function of time T after the laser pulse. The maximum electron polarization reaches $> 99\%$ after about 1.5 ms following the laser pulse. Below we investigate the coherent transfer of such well-prepared electron spin states to a neighboring ^{29}Si nuclear spin.

TABLE I: Lifetime of triplet sub-levels, for two orientations of $SL1$ centers, obtained from fitting to the flash delay curve.

EPR transition	Lifetime
$0 \rightarrow +1, SL1^0$	$(1/k_0)^0 = 2000(4) \mu s, (1/k_{+1})^0 = 280(2) \mu s$
$0 \rightarrow -1, SL1^0$	$(1/k_0)^0 = 1970(4) \mu s, (1/k_{-1})^0 = 330(2) \mu s$
$-1 \rightarrow 0, SL1^{90}$	$(1/k_{-1})^{90} = 960(2) \mu s, (1/k_0)^{90} = 200(1) \mu s$
$+1 \rightarrow 0, SL1^{90}$	$(1/k_{+1})^{90} = 987(2) \mu s, (1/k_0)^{90} = 205(1) \mu s$
$k_x = 1.6(3) ms^{-1}, k_y = 4.93(6) ms^{-1}, k_z = 0.50(4) ms^{-1}$	

For the following electron nuclear double resonance (ENDOR) experiments, we focus on four selected lev-

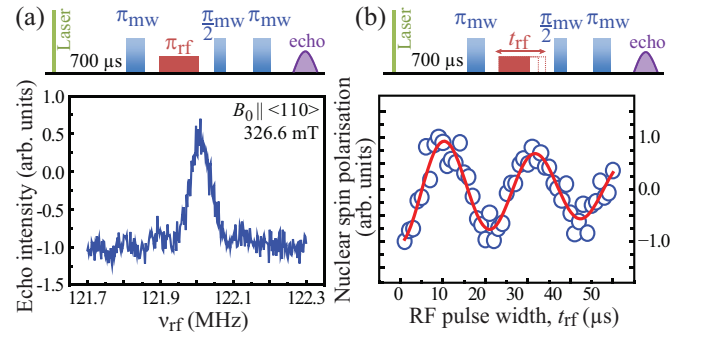


FIG. 3: (color online). (a) Davies-ENDOR spectrum illustrating the hyperfine coupling between the triplet and nearest-neighbour ^{29}Si for the $SL1^{90}$ center. (b) Rabi oscillation of the ^{29}Si nuclear spin, driven between the states $|1\rangle$ and $|2\rangle$, detected by monitoring the electron spin echo intensity.

els (labeled $|1\rangle, |2\rangle, |3\rangle$ and $|4\rangle$ in Fig. 1b) of $SL1^{90}$. We studied the hyperfine coupling strength between the ^{29}Si nuclear spin and triplet electron spin using the Davies ENDOR pulse sequence (Fig. 3a). For $SL1^{90}$, T_0 decays more quickly than T_{\pm} (see Table I), thus the states $|3\rangle$ and $|4\rangle$ are mostly unpopulated in $\sim 700 \mu s$. A selective microwave π -pulse between $|1\rangle$ and $|3\rangle$ creates a polarization across the nuclear spin transitions, which can be driven using a radiofrequency (ν_{rf}) pulse. The ENDOR signal is obtained by monitoring the electron spin echo on the $|1\rangle:|3\rangle$ transition as a function of ν_{rf} . Fig. 3a shows the $|1\rangle:|2\rangle$ transition frequency dominated by the strong hyperfine interaction. Thus, with resonant rf pulses we can selectively address ^{29}Si nuclear spins at specific lattice sites i and j . These nuclear spins can be coherently manipulated with high fidelity, as illustrated by the Rabi oscillations in Fig. 3b, in addition to being prepared and measured using the triplet electron spin.

Using a sequence based on Davies ENDOR, it is possible to coherently transfer a state of the electron spin to a coupled nuclear spin (see Ref [4] for full details). We apply this to transfer the highly polarised triplet electron spin coherence to, and from, the nearest neighbour ^{29}Si nuclear spin (see Figure 4a). The decay of the recovered spin coherence as a function of the storage time in the nuclear spin ($2\tau_n$) is shown in Fig. 4b, with an exponential decay of time-constant $0.9(1)$ ms. The measured decay is dominated by the relaxation of the T_+ sub-level back to the ground singlet state ($1/k_+ = 987 \mu s$), rather than ^{29}Si nuclear decoherence. This confirms our assignment of the decay rates shown in Table I. By subtracting k_+ from the decay in Fig. 4b we can estimate T_2 of ^{29}Si to be several milliseconds, however, it is possible to make a more accurate measurement as described below.

Using the pulse sequence shown in Fig. 4c, we shift the RF pulses within a fixed experimental window of 1 ms in order to remove the effect of the triplet relaxation and

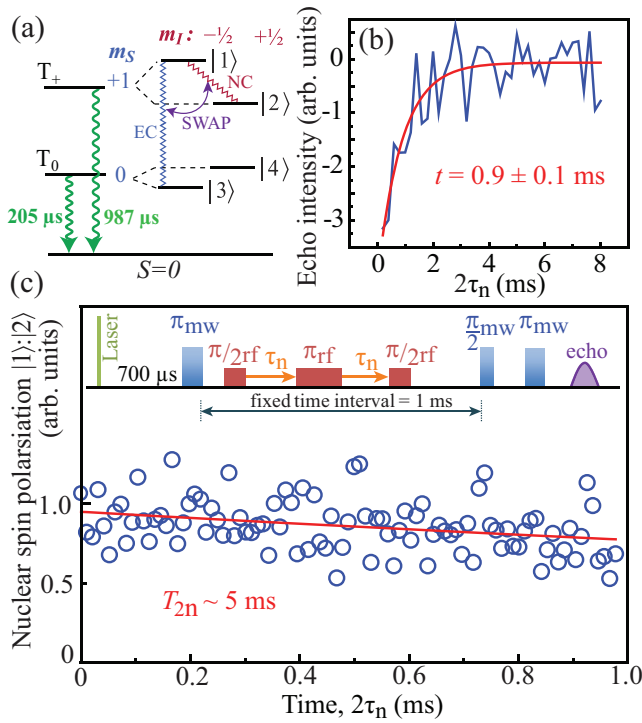


FIG. 4: (color online). (a) The electron-spin coherence (EC) of the triplet is transferred to, and from, a ^{29}Si nuclear coherence (NC). (b) The retrieved electron spin echo intensity (blue) decays as a function of the ^{29}Si nuclear storage time, $2\tau_n$. A fit to an exponential decay (red) yields a time constant of $0.9(1)$ ms, apparently limited by the lifetime (0.99 ms) of the T_+ state. (c) By fixing the experimental time window to ~ 1 ms, the intrinsic coherence time of the nuclear spin can be measured. rf pulses were phase-cycled to confirm here that the measured electron spin echos arose solely from nuclear spin coherences.

directly measure the ^{29}Si coherence time [31]. The sequence is based on Davies ENDOR described above, but with the single rf π pulse replaced with a nuclear Hahn echo sequence, whose delay time τ_n is swept. In the absence of nuclear spin decoherence, the applied rf pulses form a net 2π rotation. In contrast, when the nuclear spin is fully decohered, the nuclear spin polarisation across the $|1\rangle\langle 2|$ transition falls to zero. Fitting the data to an exponential decay gives the nuclear coherence time of $5(1)$ ms. The bulk value for T_{2n} of ^{29}Si in natural silicon has been measured by NMR and found to be 5.6 ms, limited by ^{29}Si dipolar coupling [32]. Remarkably, the nuclear spin coherence appears unaffected by strong coupling to the triplet electron spin.

In conclusion, we utilized the coupling between nuclear spin and photoexcited electron spin triplet in silicon to demonstrate the coherent storage and retrieval of triplet electron spin coherence in the ^{29}Si nuclear spin. This motivates further studies in how the nuclear spin state survives the decay to the ground singlet state, as well

as the application of NMR pulse sequences to remove the effect of nuclear spin dipolar couplings to achieve coherence times of up to 25 seconds [3]. Furthermore, given the well-developed silicon isotope engineering [33, 34] it will be possible to investigate more than one nuclear spin strongly coupled to the single electron spin in the photoexcited triplet state and explore optical control of the interaction between the nuclear spins.

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- [1] T. D. Ladd, J. R. Goldman, F. Yamaguchi, Y. Yamamoto, E. Abe, and K. M. Itoh, Phys. Rev. Lett. **89**, 017901 (2002).
- [2] K. M. Itoh, Solid State Commun. **133**, 747 (2005).
- [3] T. D. Ladd, D. Maryenko, Y. Yamamoto, E. Abe, and K. M. Itoh, Phys. Rev. B **71**, 014401 (2005).
- [4] J. J. L. Morton, A. M. Tyryshkin, R. M. Brown, S. Shankar, B. W. Lovett, A. Ardavan, T. Schenkel, E. E. Haller, J. W. Ager and S. A. Lyon, Nature **455**, 1085 (2008).
- [5] J. R. Petta, A. C. Johnson, J. M. Taylor, E. A. Laird, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Science **309**, 2180 (2005).
- [6] K. C. Nowack, M. Shafiei, M. Laforest, G. E. D. K. Prawiroatmodjo, L. R. Schreiber, C. Reichl, W. Wegscheider, and L. M. K. Vandersypen, Science **333**, 1269 (2011).
- [7] T. Obata, M. Pioro-Ladriere, Y. Tokura, Y. Shin, T. Kubo, K. Yoshida, T. Taniyama, and S. Tarucha, Phys. Rev. B **81**, 085317 (2010).
- [8] A. M. Stoneham, A. J. Fischer and P. T. Greenland, J. Phys. Cond. Mat. **15**, L447 (2003).
- [9] M. Schaffry, V. Filidou, S. D. Karlen, E. M. Gauger, S. C. Benjamin, H. L. Anderson, A. Ardavan, G. A. D. Briggs, K. Maeda, K. B. Henbest, F. Giustino, J. J. L. Morton and B. W. Lovett, Phys. Rev. Lett. **104**, 200501 (2010).
- [10] E. M. Gauger, P. P. Rohde, A. M. Stoneham and B. W. Lovett, New J. Phys. **10**, 073027 (2008).
- [11] M. Schaffry, B. W. Lovett, and E. M. Gauger, Phys. Rev. A **84**, 032332 (2011).
- [12] J. H. van der Waals, Appl. Magn. Reson. **20**, 545 (2001).
- [13] M. Deimling, H. Brunner, K. P. Dinse, K. H. Haussner, and J. P. Colpa, J. Magn. Reson. **39**, 185 (1980).
- [14] P. Bachert, H. Brunner, K. H. Haussner, and J. P. Colpa, Chem. Phys. **91**, 435 (1984).
- [15] K. Takeda, K. Takegoshi and T. Terao, J. Phys. Soc. Japan **73**, 2319 (2004).
- [16] J. Schmidt, D. J. van den Heuvel, A. Henstra, T.-S. Lin and W. Wenckebach, Pure & App. Chem. **64**, 859 (1992).
- [17] V. Filidou, S. Simmons, S. D. Karlen, H. L. Anderson, F. Giustino, J. J. L. Morton *in preparation* (2011)

- [18] G. D. Watkins, J. W. Corbett and R. M. Walker, J. Appl. Phys **30**, 1198 (1959).
- [19] J. W. Corbett, G. D. Watkins, R. M. Chrenko and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).
- [20] K. L. Brower, Phys. Rev. B **4**, 1968 (1971).
- [21] B. Stich, S. Greulich-Weber and J. M. Spaeth. J. Appl. Phys. **77**, 1546 (1995).
- [22] W. Akhtar, H. Morishita, L. S. Vlasenko, D. S. Poloskin and K.M. Itoh, Physica B **404**, 4583 (2009).
- [23] F. P. Wang, B. Monemar, Phys. Rev. B **42**, 7576 (1990).
- [24] L. S. Vlasenko, Yu. V. Martynov, T. Gregorkiewicz, and C. A. J. Ammerlaan, Phys. Rev. B **52**, 1144 (1995).
- [25] W. Akhtar, H. Morishita, K. Sawano, Y. Shiraki, L. S. Vlasenko, and K. M. Itoh, Phys. Rev. B **84**, 045204 (2011).
- [26] L. S. Vlasenko, Physica B+C **116**, 281 (1983).
- [27] L. S. Vlasenko, M. P. Vlasenko, D. S. Poloskin, R. Laiho, H. Hayashi, T. Itahashi, A. Sagara, and K. M. Itoh, Phys. Stat. Sol. (c). **3**, 12 (2006).
- [28] T. Itahashi, H. Hayashi, K.M. Itoh, D.S. Poloskin, and L.S. Vlasenko, Physica B **404**, 5054 (2009).
- [29] A. M. Frens, M. E. Braat, A. B. van Oosten and J. Schmidt, Mat. Sci. Forum, **117**, 195 (1993).
- [30] L. S. Vlasenko, I. M. Zaritskii, A. A. Konchits, B. D. Shanina, Sov. Phys. Solid State, **26**, 66 (1984).
- [31] P. Hoefer, A. Grupp and M. Mehring, Phys. Rev. A **33**, 3519 (1986).
- [32] A. E. Dementyev, D. Li, K. MacLean, and S. E. Barrett, Phys. Rev. B **68**, 153302 (2003).
- [33] K. Takyu, K. M. Itoh, K. Oka, N. Saito, and V. I. Ozhogin, Jpn. J. Appl. Phys., Part 2 **38**, L1493 (1999).
- [34] K. M. Itoh, J. Kato, M. Uemura, A. K. Kaliteevskii, O. N. Godisov, G. G. Devyatych, A. D. Bulanov, A. V. Gusev, I. D. Kovalev, P. G. Sennikov, H.-J. Pohl, N. V. Abrosimov, and H. Riemann, Jpn. J. Appl. Phys., Part 1 **42**, 6248 (2003).